

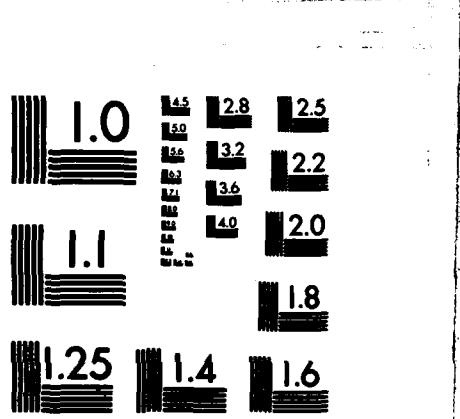
AD-A136 330 PHOTOCHEMISTRY AND PHOTOPHYSICS OF LASER DYES(U) BOSTON 1/1
UNIV MA DEPT OF CHEMISTRY G JONES 31 OCT 83 TR-8
N00014-79-C-0054

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REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER Technical Report No. 8 - final	2. GOVT ACCESSION NO.	3. RECIPIENT'S CATALOG NUMBER
4. TITLE (and Subtitle) Photochemistry and Photophysics of Laser Dyes		5. TYPE OF REPORT & PERIOD COVERED Final, 11/1/78-10/31/82
		6. PERFORMING ORG. REPORT NUMBER
7. AUTHOR(s) G. Jones, II		8. CONTRACT OR GRANT NUMBER(s) N00014-79-C-0054
9. PERFORMING ORGANIZATION NAME AND ADDRESS Department of Chemistry Boston University Boston, MA 02215		10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS NR 395-609
11. CONTROLLING OFFICE NAME AND ADDRESS Office of Naval Research Eastern/Central Regional Office 666 Summer Street, Boston MA 02210		12. REPORT DATE October 31, 1983
14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office)		13. NUMBER OF PAGES 10
		15. SECURITY CLASS. (of this report) unclassified
		16a. DECLASSIFICATION/DOWNGRADING SCHEDULE
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17. DISTRIBUTION STATEMENT (of the abstract entered in Block 26, if different from Report)		
18. SUPPLEMENTARY NOTES		
19. KEY WORDS (Continue on reverse side if necessary and identify by block number) coumarin laser dyes, "blue-green" laser dyes, dye photodegradation, medium effects on laser dyes, coumarin emission yields		
20. ABSTRACT (Continue on reverse side if necessary and identify by block number) Results of a study of photophysical properties and mechanisms of photo-degradation of coumarin dyes are summarized. Discussion includes effects of polar media on dye emission yield and lifetime, solubilization of dyes in water with surfactants, products of dye photodegradation, electron transfer properties of coumarin dyes, mechanisms of dye photodecomposition, and recommendations of restorative procedures for dye media.		

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PHOTOCHEMISTRY AND PHOTOPHYSICS OF LASER DYES

INTRODUCTION

The present research program began November 1, 1978 as an outgrowth of work in organic photochemistry on sensitizing dyes and mechanisms of photoinduced isomerization reactions which was supported earlier by the Office of Naval Research. The program encompassed the original 12-month contract (N00014-79-C-0054), two funded renewals, and an extension period which ended, October 31, 1982. Experimental work related to the program continued until June, 1983, and manuscript and report preparation extended to November, 1983.

The objectives of the program involved a thorough investigation of photophysical and photochemical properties of the important "blue-green" coumarin laser dyes directed to the improvement of service life and lasing efficiency of dye media. The proposed studies included measurement of the important photophysical parameters for a variety of dye structures with emphasis on medium effects on fluorescence quantum yields and lifetimes for the coumarins and the determination of the yields of dye triplets and their properties. Other goals involved the identification of photoproducts obtained on degradation of dyes under steady illumination. Mechanisms of degradation were also to be assigned where possible and recommendations set forth concerning minimization of decomposition.

Other lines of research included evaluation of dye properties in aqueous media with emphasis on the possibilities of solubilization of dyes



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using surfactant additives and the development of media having advantages of reduced optical inhomogeneity under lasing conditions. The effects of quenchers of dye excited states were also of interest in terms of establishing the types of additives which might stabilize dye media to photodegradation.

ACHIEVEMENTS OF THE PROGRAM

The program was successful in providing new information and recommendations concerning each of the objectives outlined above. A brief summary is provided here with references to papers which have been published or recently submitted and the appropriate technical reports to ONR. Structures 1 - 11 identify most of the coumarin dyes which were included in our investigations.

(1) A study of the quantum yields of fluorescence and singlet lifetimes (the latter determined by time-correlated singlet-photon counting) for structures 1 - 7 established the importance of a rotatory non-radiative decay path which is important for selected dyes in polar media. The important structural feature, the unnumbered amine group at the 7-position, and the evolution of excited species in terms of planar and twisted intramolecular charge transfer states, 12 and 13 were identified.²

(2) The red shifts of absorption and emission bands of coumarin dyes in solvents of high polarity were investigated. The solvatochromism provided linear correlations with well known solvent parameters which reflect general polarity-polarisability and hydrogen bonding properties of organic media. The quite regular dependences can be helpful in "solvent tuning" of

the wavelength of emission (lasing).³

(3) An investigation of quenching of coumarin singlets and triplets by electron transfer agents (both donors and acceptors) was carried out. Redox potentials determined by cyclic voltammetry, rate constants for bimolecular quenching of excited dye, and transient absorption obtained by flash photolysis were used to determine that coumarin dyes have a moderate tendency to interact with either electron donors or acceptors. These observations will be helpful in selecting additives (quenchers) which may enhance stability without leading to unwanted new photochemistry.³

(4) A previously unreported phenomenon, the concentration (self) quenching of fluorescence for coumarins 1 - 4, was observed. A correlation was further made between bimolecular self reaction of excited dye with the quantum yield of photodegradation. The singlet coumarin excited state was identified as primarily responsible for photodecomposition which leads to dealkylation (loss of amine substituent groups - e.g., 2 \rightarrow 6). The largely unreactive triplet state was observed by flash photolysis and its unimolecular and bimolecular decay rate parameters determined.⁴

(5) A more comprehensive examination of solvent effects on fluorescence lifetime and quantum yield revealed that certain dyes which are "non-rigid" with respect to the amine group, 8 - 11, are relieved of the quantum wasting non-radiative rotatory decay prevalent in polar media (vide supra) due to subtle structural features which could be outlined in detail. New theory regarding rotatory decay of polar excited states was developed with emphasis on the role of local excited state bond orders. Emission properties in low temperature glasses, deuterated solvents (including

water) and triplet state properties for representative dyes were also evaluated.⁶

(6) The effects of surfactants in solubilizing hydrophobic coumarin dyes in water were established. Cationic and anionic detergents as well as cyclodextrins were effective in producing moderately concentrated aqueous dye solutions which, in some cases, were strongly emissive. Emission properties, photodegradation, interaction with quenchers, and flash photochemistry of solubilized coumarins were investigated.⁶

(7) New products of coumarin photodegradation were identified. A path for decomposition involving reduction of the coumarin double bond (3-position) and a photooxidation involving the amine moiety for a rigid dye (4) were established. Intersystem crossing yields (by triplet counting) were determined and a mechanism for coumarin photolysis involving singlet dye and the production of radicals was proposed.⁷

WORK IN PROGRESS AND FUTURE DEVELOPMENTS

Additional experiments involving the dependence of coumarin absorption and emission on medium are currently underway. These results will lead to further parameterization of solvent and emission (lasing) properties and will be the subject of a future publication. Studies are also underway involving the observation of chemically induced dynamic nuclear polarization (CIDNP) for dye solutions during photolysis. This investigation, carried out with the collaboration of Dr. J. Bargon of IBM Research Laboratories, San Jose, is directed to unambiguous identification of proposed radical intermediates which are responsible for photodegradation.

A series of experiments is planned around a new dye laser facility at Boston University. As the result of a recent DOD instrument grant, a Nd/YAG pumped dye laser (Quantel Datachrom 5000) has been purchased and will be used to determine photostability of dyes under lasing conditions. The facility will allow investigation of dyes under intense flashlamp illumination (>150 mJ/8 ns pulse @ 10 Hz) for product studies and for transient detection of absorption (LeCroy 100 MHz transient digitizer and CAMAC/LSI computer interface). Depending on the availability of funds, the program will continue with emphasis on the following themes:

- (1) identification of transient intermediates such as radicals or radical-ions which induce dealkylation, net redox reaction, or polymerization of laser dyes
- (2) the behavior of dyes in "unusual" media: surfactant solutions, cyclodextrin and other inclusion complexes; "protection" of dye structure and sustained emission in microheterogeneous media
- (3) the design and synthesis of laser dyes for the ultraviolet (300-400 nm) with emphasis on the fundamentals of photolysis mechanism and non-radiative decay (rotatory paths, electron transfer) established in the coumarin study
- (4) the discovery of multiple photon photochemical processes for laser dyes under high intensity flashlamp illumination (lasing conditions)

PERSONNEL

Principal Investigator

Guilford Jones, II, Professor of Chemistry, Boston University
(1978-83)

Postdoctoral Research Associates

W. R. Jackson (Ph. D., U. of California, Santa Cruz): December 1,
1978 through December 31, 1980; now at IBM Research Laboratory, E.
Fishkill, New York

W. R. Bergmark (Ph. D., Massachusetts Institute of Technology,
Professor of Chemistry, Ithaca College): June 15, 1982 through
October 31, 1982; returned to Ithaca College after sabbatical year
at Boston University

Graduate Student

S. F. Griffin (B. S., U. of Massachusetts): January - June, 1983;
continuing in the Ph. D. program at Boston University

Undergraduate Student

C. Choi (B. A., Boston University, 1981): January, 1980 through August, 1981; presently a graduate student in Ph. D. program, U. of Chicago

Senior Collaborator

A. M. Halpern (Associate Professor of Chemistry, Northeastern University): assisted with fluorescence lifetime measurements during 1979-81

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5. Technical Report No. 5, October 31, 1983

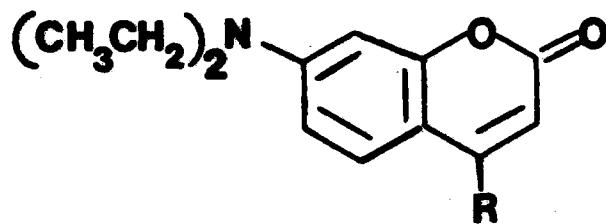
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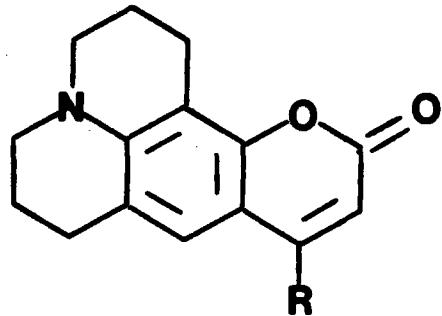
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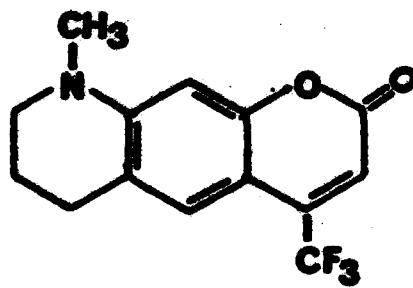
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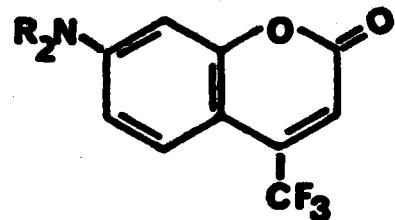


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4, $\text{R} = \text{CF}_3$

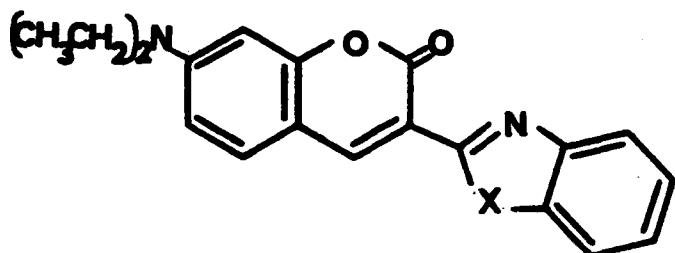


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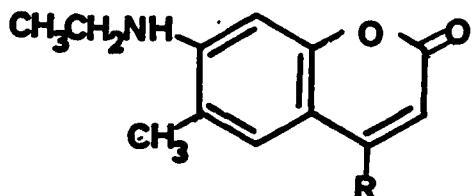


6, $\text{R} = \text{H}$

7, $\text{R} = \text{CH}_3$



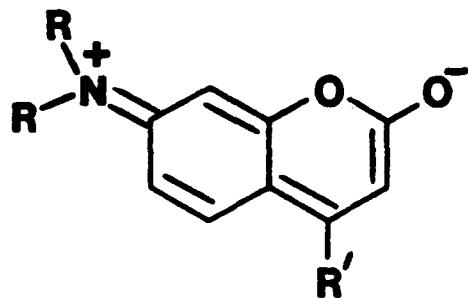
8, $\text{X} = \text{S}$



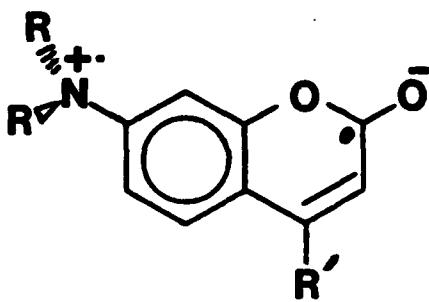
10, $\text{R} = \text{CH}_3$

9, $\text{X} = \text{NCH}_3$

11, $\text{R} = \text{CF}_3$



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